

Restoring the density-gradient expansion for exchange in solids and surfaces

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Successful modern generalized gradient approximations (GGA's) are biased toward atomic energies. Restoration of the first-principles gradient expansion for exchange over a wide range of density gradients eliminates this bias. We introduce PBEsol, a revised Perdew-Burke-Ernzerhof GGA that improves equilibrium properties of densely-packed solids and their surfaces.

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Ground-state Kohn-Sham density functional theory (DFT) [1] has been hugely successful for electronic structure calculations of solids and molecules. Its accuracy relies upon good approximations to the unknown exchange-correlation (xc) energy as a functional of the electronic spin densities[2]. Over the past four decades, a variety of increasingly sophisticated approximations has been developed[3]. The most commonly used in solid-state calculations today is the PBE version[4] of the generalized gradient approximation (GGA), employing both the density and its gradient at each point in space. Popular GGAs represent a well-tempered balance between computational efficiency, numerical accuracy, and reliability, but PBE also juggles the demands of quantum chemistry and solid-state physics[5].

While PBE represented a high-point of non-empirical functional development 11 years ago, much has since been learned about its limitations. PBE reduces the chronic overbinding of the local spin density approximation (LSDA)[1] but, while LSDA often slightly underestimates equilibrium lattice constants by about 1%, PBE usually overestimates them by about the same amount. Other equilibrium properties, such as bulk moduli, phonon frequencies, magnetism, and ferro-electricity, are sensitive to the lattice constant, and so are also overcorrected by PBE[6]. Surface energies are too low in LSDA, but are made lower still by PBE[7].

However, attempts to construct a better GGA face a Procrustean dilemma[8]: Those with an enhanced gradient dependence[9, 10] improve atomization and total energies, but worsen bond lengths, while more recent suggestions of a GGA for solids and surfaces[6, 11, 12, 13, 14, 15] have a reduced gradient dependence and typically do improve lattice parameters and/or surface energies, but have been criticized for worsening energetics[13]. More advanced functionals have been constructed. For example, meta-GGA's, using also the orbital kinetic-energy densities, provide greater accuracy over a wider range of systems and properties[3]. But current meta-GGA's do

not improve lattice constants as dramatically as surface energies, and meta-GGA's are not yet available in all solid-state codes.

In the present work, we explain the origin of this dilemma and show that, in a sense, *no* GGA can do both: Accurate atomic exchange energies require violating the gradient expansion for slowly-varying densities, which is valid for solids and their surfaces. At the GGA level, one must choose. A pragmatic approach to lattice properties is therefore to use a modified functional especially for solids which, unlike previous suggestions, recovers the gradient expansion for exchange. Such a functional becomes exact for solids under intense compression. Analogous reasoning for correlation suggests fitting the jellium xc surface energy, as was first done by Armiento and Mattsson[12]. Our variation on PBE satisfies these new conditions, by simply altering two parameters in the original formula. We find our new functional significantly improves most lattice constants and surface energies while worsening atomization energies (as does AM05 of Ref. [12]). By restoring the gradient expansion, PBEsol also yields excellent jellium surface exchange energies, and provides an improved starting point for more advanced functional construction.

The GGA form for the exchange energy is simply

$$E_x^{\text{GGA}}[n] = \int d^3r e_x^{\text{unif}}(n(\mathbf{r})) F_x(s(\mathbf{r})) \quad (1)$$

where $n(\mathbf{r})$ is the electronic density, $e_x^{\text{unif}}(n)$ is the exchange energy density of a uniform electron gas (proportional to $n^{4/3}$), $s = |\nabla n|/(2k_F n)$ (with $k_F = (3\pi^2 n)^{1/3}$) is the dimensionless density gradient, and $F_x(s)$ is the so-called enhancement factor for the given GGA[4]. Eq. (1) is the spin-unpolarized form, from which the spin dependence can be deduced[2]. Any GGA that recovers the uniform gas limit has

$$F_x(s) = 1 + \mu s^2 + \dots \quad (s \rightarrow 0) \quad (2)$$

The gradient expansion[1] that is accurate for slowly-varying electron gases has[16] $\mu_{GE} = 10/81 \approx .1234$.

To begin, Ref [17] showed that the exchange energies of neutral atoms are very well approximated by their asymptotic expansion for large Z , i.e., $E_x = -.2208Z^{5/3} - .196Z + \dots$. The first term arises from LSDA, but the second arises in a GGA from the s^2 contribution to Eq. (2) and requires $\mu \approx 2\mu_{GE}$. Thus any GGA that is accurate for the exchange energies of neutral atoms must have $\mu \approx 2\mu_{GE}$. PBE does, although its value of $\mu = 0.219$ was found from a different non-empirical argument. So does B88, as it was fitted to the x energies of noble gas atoms[18]. Even PW91 essentially does too[19], as only at irrelevantly small values of s does it revert to μ_{GE} .

Thus, to attain accurate exchange energies of atoms (vital to dissociation energies in molecules and cohesive energies in solids), any GGA must strongly violate the gradient expansion for slowly-varying densities[17]. But most of thermochemistry occurs without free atoms, and is not much worse in LSDA than in PBE (e.g., [20]). Moreover, for the evaluation of exchange, the densities of real solids and their surfaces are often almost slowly-varying over space. Restoring the gradient expansion should improve their description (but worsen atomization energies). The GGA is a limited form, and *cannot* satisfy both conditions. Eq. (2) suggests a necessary condition for convergence of the second-order gradient expansion for exchange: $s \lesssim 1$. Since $s \lesssim 1$ for valence electrons in densely-packed solids (or $s \lesssim 2$ in core-valence regions of alkali atoms), and since the reduced Laplacian of the density is also $\lesssim 1$, the gradient expansion is important for exchange in solids. We choose μ_{GE} for PBEsol.

Now, for a GGA correlation functional that recovers the uniform gas limit, the gradient expansion is

$$E_c[n] = \int d^3r n(\mathbf{r}) \{ \epsilon_c^{\text{unif}}(n(\mathbf{r})) + \beta t^2(\mathbf{r}) + \dots \} \quad (3)$$

where $\epsilon_c^{\text{unif}}(n)$ is the correlation energy per particle of the uniform gas, β is a coefficient, and $t = |\nabla n|/\{2k_{TF}n\}$ is the appropriate reduced density gradient for correlation (fixed by the Thomas-Fermi screening wavevector $k_{TF} = \sqrt{4k_F/\pi}$, not k_F .) For slowly-varying high densities[21], $\beta_{GE} = 0.066725$. Unlike exchange, the second-order term in the gradient expansion for correlation cannot be small compared to the local term everywhere even for valence electrons in solids: βt^2 can be large compared to $|\epsilon_c^{\text{unif}}|$ (as $\beta_{GE}t^2 = 0.1s^2/r_s$). The gradient expansion can be relevant to real systems (especially solids) for exchange, but much less so for correlation.

The gradient expansion for correlation is less relevant to solids than is $f_{xc}(q)$ for the response of the uniform gas to a weak potential $\lambda \cos(\mathbf{q} \cdot \mathbf{r})$. The exact $f_{xc}(q)$ is almost independent of q , up to $2k_F$ [22]. Thus LSDA, which produces a constant (the value at $q = 0$), yields an accurate approximation for $q \lesssim 2k_F$. But any GGA

with a non-zero xc contribution to second order in ∇n produces a term quadratic in q . Since we are interested in weakly-varying valence electron densities in densely-packed solids, we wish to retain this excellent feature of LSDA. If

$$\mu = \pi^2\beta/3, \quad (4)$$

there is complete cancellation between beyond-LSDA x and c contributions, restoring LSDA response.

In PBE, the gradient expansion for correlation is respected, i.e., $\beta = \beta_{GE}$, and $\mu \approx 2\mu_{GE}$ satisfies Eq. (4). This choice agrees well with the PW91 exchange functional, and the numerical real-space cutoff construction[19] of the GGA exchange energy, and yields highly accurate exchange energies of atoms. But we have already argued that $\mu \approx 2\mu_{GE}$ is harmful for many condensed matter applications. Once we choose μ_{GE} for exchange, we cannot recover simultaneously the GEA for correlation and the linear response of LSDA for a uniform density. Exact satisfaction of Eq. (4) would yield $\beta = 0.0375$, but an increased value will satisfy another, more relevant constraint for solid-state applications.

For correlation, large neutral jellium clusters are our paradigm, for which $E_{xc} \rightarrow e_{xc}^{\text{unif}}V + e_{xc}^{\text{surf}}A + \dots$ as the radius grows, where e_{xc}^{surf} is the jellium surface xc energy, V the volume of the cluster and A its area. A GGA that recovers e_{xc}^{surf} will be correct in leading- and next-order for neutral jellium clusters as $N \rightarrow \infty$, in a similar way to modern exchange GGA's for neutral atoms. Moreover, the surface energy is dominated by xc contributions and e_{xc}^{surf} is really a bulk-like property, arising mainly (103% at $r_s = 2$) from a moderately-varying-density region (with $s \lesssim 1$) inside the classical turning plane.

We check that this condition is compatible with the restoration of the gradient expansion for exchange. Because jellium clusters have a uniform bulk density and because most of the surface energy comes from within, the gradient expansion should be accurate. We find, at bulk density $r_s = 3$, the errors of the surface exchange energy are: LSDA 27%, PBE -11% and PBEsol 2.7%.

We next follow the lead of Ref. [12], and fit e_{xc}^{surf} to determine our correlation functional. But the jellium e_{xc}^{surf} is not known exactly. Figure 1 shows surface energy enhancements relative to LSDA. The likely "range of the possible" for e_{xc}^{surf} extends from TPSS meta-GGA [3, 7] or RPA+ [23] at the low end of what is possible (in agreement with the most recent Quantum Monte Carlo calculations[24]) to the RPA-like Pitarke-Perdew (PP)[25] value at the high end. The TPSS value probably provides the best value that a GGA should try to achieve. We choose $\beta = 0.046$ and $\mu = \mu_{GE}$ (within the PBE form) for PBEsol, to best fit the TPSS results. PBEsol should improve most surface energies over LSDA, whereas PBE worsens them.

Thus we have violated Eq. (4) in favor of good surface energies. But our value for β is considerably closer

FIG. 1: Ratio of calculated surface exchange-correlation to that of LSDA as a function of r_s for various approximations.

to that of the linear response requirement (0.037) than that demanded by complete restoration of the gradient expansion (0.066). The linear response of PBEsol is reasonably close to that of LSDA, and closer than that of the gradient expansion.

FIG. 2: Enhancement factors of PBE and PBEsol, for spin-unpolarized systems, as a function of reduced density gradient, for various values of r_s .

PBEsol is exact for the uniform gas, and highly accurate for large jellium clusters, both of moderate and high

density. But PBEsol also becomes exact for solids under intense compression, where real solids and their surfaces become truly slowly-varying, and exchange dominates over correlation[17]. In Fig. 2, we plot the enhancement factors of PBE and PBEsol. For a spin-unpolarized ($\zeta = 0$) density $n = 3/(4\pi r_s^3)$, we define $F_{xc}(r_s, s)$ by

$$E_{xc}^{\text{GGA}}[n] = \int d^3r e_x^{\text{unif}}(n(\mathbf{r})) F_{xc}(r_s(\mathbf{r}), s(\mathbf{r})) \quad (5)$$

The high-density ($r_s \rightarrow 0$) limit is $F_x(s)$ of Eq. (1). The nonlocality or s -dependence of GGA exchange is diminished from PBE to PBEsol, making the latter somewhat closer to LSDA. Over the whole range $s \lesssim 1$, the PBEsol F_x is close to $1 + \mu_{GE}s^2$. The range $0 \lesssim s \lesssim 3$ is energetically important for most properties of most real systems, while $0 \lesssim s \lesssim 1$ and $1 < r_s < 10$ are the ranges for valence-electron regions in many densely-packed solids.

class	LSDA	PBE	TPSS	PBEsol
mean error				
4 simple metals	-9.0	2.9	5.3	-0.3
5 semiconductors	-1.1	7.9	6.2	3.0
5 ionic solids	-8.4	8.5	6.8	2.0
4 transition metals	-4.0	6.4	2.5	0.0
total	-5.5	6.6	5.4	1.3
mean absolute error				
4 simple metals	9.0	3.4	5.3	2.3
5 semiconductors	1.3	7.9	6.2	3.0
5 ionic solids	8.4	8.5	6.8	2.7
4 transition metals	4.0	6.4	2.7	1.9
total	5.6	6.7	5.4	2.5

TABLE I: Errors in equilibrium lattice constants (in $\text{\AA} \times 10^{-2}$) on our data set of 18 solids, relative to experiment with estimates of the zero-point anharmonic expansion removed[26].

To test our functional, we employ a test set of 18 solids from Ref [26]. These come in four groups: Simple metals (Li,Na,K,Al), semiconductors (C,Si,SiC,Ge,GaAs), ionic solids (NaF,NaCl,LiCl,LiF,MgO), and transition metals (Cu,Rh,Pd,Ag). The set is not claimed to be representative, but was chosen for the availability of basis functions and anharmonic corrections[26]. Our calculations use the Gaussian orbital periodic code of Ref [26], with basis sets of the same or higher quality. In Table I, we list both the mean errors and the mean absolute errors for lattice constants in LSDA, PBE, TPSS, and PBEsol. With the sole and marginal exception of SiC, LSDA makes lattice constants too short, as indicated by the negative mean errors. With the sole and marginal exception of Na, PBE makes lattice constants too long. Overall, the systematic PBE overestimate is close to the systematic LSDA underestimate, as shown by the total mean absolute errors, and TPSS cures this very little. On the other hand, PBEsol greatly reduces this overestimate, by a factor of almost 4,

except for semiconductors, where LSDA is unsurpassed.

error	LSDA	PBE	TPSS	PBEsol
mean error	3.35	0.54	0.18	1.56
mean abs. error	3.35	0.67	0.26	1.56

TABLE II: Errors in atomization energies (eV) for the AE6 set of molecules, using the 6-311+G(3df,2p) basis set.

PBEsol is not expected to give good atomization energies. In Table 2, we give the errors on the AE6 data set of molecules. These 6 molecules (SiH_4 , S_2 , SiO , C_3H_4 (propyne), $\text{C}_2\text{H}_2\text{O}_2$ (glyoxal), and C_4H_8 (cyclobutane)) were chosen[27] to be representative, i.e., to reproduce the errors of much larger data sets. As is clear, and expected, PBEsol is much less accurate than PBE, only about halving the error of LSDA. This can be largely attributed to PBEsol's worsened total energies of atoms. For these atoms, the typical error in the total energy per electron is 0.2-0.3 eV for PBE, but 1.1-1.3 eV for PBEsol.

We have demonstrated the relevance of the second-order gradient coefficient for the exchange energy of a slowly-varying density to the bulk and surface properties of solids. The TPSS meta-GGA [3], which incorporates this coefficient, gets good surface energies but its lattice constants are only marginally better than those of PBE on which it builds, whereas PBEsol is significantly better. This suggests that an improved meta-GGA might need to recover the gradient expansion for exchange over a wider range of $n(\mathbf{r})$ than TPSS does.

Previous attempts to improve on PBE within the GGA form have retained the PBE gradient coefficients μ and β for small s , but altered the behavior at large s [6, 9, 10, 15], or have zeroed out μ [11, 12], and are thus fundamentally different from PBEsol. The AM05[12] functional performs very similarly to PBEsol for the solids studied here, but AM05 follows the proposal of Vitos et al.[11] to fit the exchange energy density of an Airy gas (noninteracting electrons in a linear potential, LAG). This is not a model solid or surface density in any global sense. This approach does not recover the gradient expansion for exchange, because the energy density has no such expansion[28]. For $r_s = 2$ to 6, LAG has errors of 11 to 56% for e_x^{surf} , compared to 1.6 to 4.1% for PBEsol. By retaining the PBE form[4], PBEsol also correctly retains the Lieb-Oxford bound and the high-density limit for correlation, while AM05 does not. Numerical comparisons and details are available [29].

We have identified the simple exchange-correlation physics underlying many properties of many solids, and shown how it differs from that for atoms. We recommend PBEsol for the applications discussed here. Any existing code that implements PBE can be instantly modified to try PBEsol, by simply replacing the values of μ and β . Modified PBE subroutines are available from <http://dft.uci.edu>. We expect geometries and related

properties to be significantly improved over PBE, especially for solids under compression. New pseudopotentials, compatible with PBEsol, must be generated to use PBEsol with pseudopotential codes. We thank NSF (CHE-0355405, CHE-0457030, and DMR-0501588) and OTKA for support.

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